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(54) Fabric care compositions

(57) There is provided a method for preventing or reducing the fading of colour on fabric by means of a divalent salt. Compositions which provide care to the color of fabrics and comprising a dye fixing agent and the divalent salt are also herein provided.

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Description**Technical field of the invention**

5 [0001] There is provided a composition which provides care to the treated fabrics, in particular color protection, especially after multiple wash cycles.

Background of the invention

10 [0002] The domestic treatment of colored fabric is a problem known in the art to the formulator of laundry compositions. Hence, it is well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering 15 operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles.

[0003] Deterioration of fabric integrity and appearance can manifest itself in several ways. Short fibers are dislodged from woven and knit fabric/textile structures by the mechanical action of laundering. These dislodged fibers may form lint, fuzz or "pills" which are visible on the surface of fabrics and diminish the appearance of newness of the fabric. Further, repeated laundering of fabrics and textiles, especially with bleach-containing laundry products, can remove dye 20 from fabrics and textiles and impart a faded, worn out appearance as a result of diminished color intensity, and in many cases, as a result of changes in hues or shades of color.

[0004] Accordingly, the problem of formulating laundry compositions which reduces the amount of dyes released from coloured fabrics upon wet treatment is a particular challenge to the formulator. This problem is now even more acute 25 with the trends of consumers to move towards more colored fabrics.

[0005] Numerous solutions have been proposed in the art to solve this problem such as by treating the fabric with a dye scavenger during the washing process as exemplified by EP 0,341,205, EP 0,033,815 or with a polyvinyl substance as exemplified by WO 94/11482. However, all these solutions are focused on preventing the end result of the dye bleeding, that is the redeposition of the dye on the fabrics. It is now an object of the invention to take the problem of dye at 30 one of its source, that is to the colour fading arising from the bleeding of the dye due to its poor fabric substantivity, especially after multiple washings.

[0006] Solutions may be found for use in the industrial treatments. However, these solutions are not usually transposable to domestic treatments. Indeed, in industrial processes a strict control over parameters such as pH, electrolyte concentration, water hardness, temperature, etc.. is possible whereas in a domestic washing machine, such a high level 35 of control is not possible.

[0007] In addition, in a domestic process, and in particular in a domestic rinse process, it is not practical to rely on high treatment temperatures such as those used in industrial processes, that is of above 40°C. Furthermore, industrial processes use high concentrations of fixing agents which is required for industrial scale treatment whilst for domestic treatment a low level is most preferred for economical reasons.

[0008] Accordingly, notwithstanding the advances in the art, there is still a need for an efficient and economical composition which provides effective reduction of the amount of dyes released from colored fabrics upon subsequent wet domestic treatments.

[0009] EP462806 provides the use of a cationic dye fixing agent in domestic treatment which assist in binding the loosely held dye to the fabric. However, whilst efficient, it has been found that the fading of fabrics still occurred to a certain degree, especially after multiple wash cycles.

[0010] Accordingly, it is therefore an advantage of the invention to provide compositions with effective dye fixing properties.

[0011] Another advantage of the invention is that such compositions provide a synergistic increase in performance of the above mentioned benefit.

[0012] A further advantage of the invention is that the treated fabrics will thereafter show a reduced tendency in the subsequent wash to release dye. Such benefit is more particularly seen after multi-wash cycles (e.g. 20 wash cycles).

Summary of the invention

55 [0013] The present invention relates to a colour care composition comprising a dye fixing agent and a divalent salt.

[0014] In another aspect of the invention, there is provided the use and method thereof for preventing or reducing the colour fading of fabrics by means of the divalent salt.

Dye fixing agent

[0015] Dye fixing agent is an essential component of the invention composition. Dye fixing agents, or "fixatives", are well-known, commercially available materials which are designed to improve the appearance of dyed fabrics by minimizing the loss of dye from fabrics due to washing. Not included within this definition are components which are fabric softeners or those described hereinafter as amino-functional polymers.

[0016] Many dye fixing agents are cationic, and are based on various quaternized or otherwise cationically charged organic nitrogen compounds. Cationic fixatives are available under various trade names from several suppliers. Representative examples include: CROSCOLOR PMF (July 1981, Code No. 7894) and CROSCOLOR NOFF (January 1988, Code No. 8544) from Crosfield; INDOSOL E-50 (February 27, 1984, Ref. No. 6008.35.84; polyethyleneamine-based) from Sandoz; SANDOFIX TPS, which is also available from Sandoz and is a preferred polycationic fixative for use herein and SANDOFIX SWE (cationic resinous compound), REWIN SRF, REWIN SRF-O and REWIN DWR from CHT-Beitlich GMBH, Tinfix® ECO, Tinfix® FRD and Soltin® available from Ciba-Geigy.

Other cationic dye fixing agents are described in "Aftertreatments for improving the fastness of dyes on textile fibres" by Christopher C. Cook (REV. PROG. COLORATION Vol. 12, 1982). Dye fixing agents suitable for use in the present invention are ammonium compounds such as fatty acid - diamine condensates e.g. the hydrochloride, acetate, metosulphate and benzyl hydrochloride of oleyldiethyl aminoethylamide, oleylmethyl-diethylenediaminemethosulphate, monostearyl-ethylene diaminotrimethylammonium methosulphate and oxidized products of tertiary amines; derivatives of polymeric alkylamines, polyamine-cyanuric chloride condensates and aminated glycerol dichlorohydrins.

Preferred dye fixing agents are the cellulose reactive dye fixing agents.

[0018] By "cellulose reactive dye fixing agent", it is meant that the agent reacts with the cellulose fibers upon heat treatment. The agents suitable for use herein can be defined by the following test procedure, so called cellulose reactivity test measurement.

25 Cellulose reactivity test measurement

[0019] Two pieces of bleeding fabrics (e.g. 10 x 10 cm of knitted cotton dyed with Direct Red 80) are soaked for 20 minutes in an aqueous solution of 1% (w/w) of the cellulose reactive dye fixing agent candidate. The pH of the solution is as it is obtained at this concentration.

[0020] The swatches are then dried. One of the dried swatches as well as an unsoaked swatch (control 1) are passed 10 times through an ironing calendar set on a linen setting.

00211 A control 2 swatch is also used in this measurement test which is a non-soaked and non-ironed swatch.

[0022] The 4 swatches are washed separately in Launder-o-meter pots under typical conditions with a commercial detergent used at the recommended dosage for ½ hour at 60°C, followed by a thorough rinsing of 4 times 200 ml of cold water and then line dried.

[0023] The wash-fastness is then measured on the swatches by determination of their so-called delta-E values versus a new, untreated swatch. Delta E's are defined, for instance, in ASTM D2244. Delta E is the computed color difference as defined in ASTM D2244, i.e. the magnitude and direction of the difference between two psychophysical color stimuli defined by tristimulus values, or by chromaticity coordinates and luminance factor, as computed by means of a specified set of color-difference equations defined in the CIE 1976 CIELAB opponent-color space, the Hunter opponent-color space, the Friele-Mac Adam-Chickering color space or any equivalent color space.

[0024] Accordingly, the lower the Delta E versus new, the better the wash fastness improvement.

[0025] If the washfastness improvement of the ironed-soaked swatch is better than that of the non-ironed soak swatch and also better than the two respective control 1 and 2, then the candidate is a cellulose reactive dye fixing agent for the purpose of the invention.

[0026] Typical cellulose reactive dye fixing agents are products containing the reactive group of the reactive dye classes selected from halogeno-triazine products, vinyl sulphones compounds, epichlorhydrine derivatives, hydroxyethylene urea derivatives, formaldehyde condensation products, polycarboxylates, glyoxal and glutaraldehyde derivatives and mixtures thereof.

[0027] Other reactive functionalities for cellulose can be found in Textile processing and properties. Elsevier (1997) from Tyrone L. Vigo at page 120 to 121, which provides the use of specific electrophilic groups with cellulose affinity.

[0028] Preferred hydroxyethylene urea derivatives include dimethylolhydroxyethylene, urea, and dimethyl urea glyoxal.

[0029] Preferred formaldehyde condensation products include the condensation products derived from formaldehyde and a group selected from an amino-group, an imino-group, a phenol group, an urea group, a cyanamide group and an aromatic group. Commercially available compounds among this class are Sandofix WE 56 from Clariant, Zetex E from Zeneca and Levogen BF from Bayer.

[0030] Preferred polycarboxylates derivatives include butane tetracarboxylic acid derivatives, citric acid derivatives,

polyacrylates and derivatives thereof.

[0031] A most preferred cellulosic reactive dye fixing agents is one of the hydroxyethylene urea derivatives class commercialised under the tradename of Indosol CR from Clariant. Still other most preferred cellulosic reactive dye fixing agents are commercialised under the tradename Rewin DWR and Rewin WBS from CHT R. Beilich.

5 [0032] Among the dye fixing agents disclosed, the preferred agent for use in the present invention are cationic, in particular polycationic dye fixing agents.

[0033] A typical amount of the dye fixing agent to be employed in the composition of the invention is from 0.01 % to 50% by weight, preferably from 0.01 % to 25% by weight, more preferably from 1 % to 10% by weight, most preferably from 1.5% to 5% active by weight of the composition.

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Divalent salt

[0034] A divalent salt is an essential ingredient of the invention. By use of this ingredient, the fabric appearance, in particular the color protection of the fabrics, is improved. Not to be bound by theory, it is believed that the salt acts by reducing the dye solubility.

15 [0035] A divalent salt is defined as a salt which in water dissociates and releases a metal ion with a valence of two.

[0036] The salt useful in the present invention is made of earth alkaline metal, and is a compound that can form hydrates upon crystallization. Typically, the salt for use in the present invention have the following formula: AM; wherein A is a cation. This cation is an earth alkaline metal, preferably selected from magnesium, calcium, more preferably 20 magnesium, and

wherein M is a counterion selected from sulfate, chloride, nitrate, carbonate, borate, and carboxylates.

[0037] Preferred salts are salts selected from magnesium, calcium and mixtures thereof; more preferably salt of magnesium.

[0038] Particularly preferred salts for use herein are selected from magnesium sulphate, magnesium bicarbonate, magnesium chloride, magnesium borate, magnesium citrate, and mixtures thereof, more preferably are selected from magnesium sulphate, magnesium chloride and mixtures thereof.

25 [0039] A typical amount of the divalent salt to be employed in the composition of the invention is from 0.01 % to 90% by weight, preferably from 0.5% and 90%, more preferably between 1% and 20%, most preferably between 3% and 10%, by weight of the composition.

30 [0040] For the purpose of the invention, it is preferred to have a weight ratio of the divalent salt to dye fixing agent greater than 1:1.

Colour care component

35 [0041] The fabric care compositions may also comprise one or more of the following colour care component:

Amino-functional polymer

[0042] Amino-functional polymers advantageously provide care to the colors of fabrics. Not included within this definition are components which are polymers as defined herein before or those described hereinafter as dye fixing agents.

40 [0043] The amino-functional polymers suitable for use in the present invention are water-soluble or dispersible, polyamines. Typically, the amino-functional polymers for use herein have a molecular weight between 150 and 10⁶, preferably between 600 and 20,000, most preferably between 1000 and 10,000. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. Preferably, the polyamine backbones described herein are modified in such a manner that at least one, preferably each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

45 [0044] For the purposes of the present invention the term "modification" as it relates to the chemical structure of the polyamines is defined as replacing a backbone - NH hydrogen atom by an R' unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an R' unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution is preferably accompanied by oxidation or quaternization of at least one backbone nitrogen.

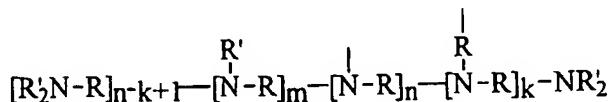
50 [0045] The linear or non-cyclic polyamine backbones that comprise the amino-functional polymer have the general formula:



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[0046] The cyclic polyamine backbones that comprise the amino-functional polymer have the general formula:

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[0047] The above backbones prior to optional but preferred subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

[0048] For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure



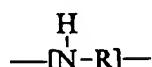
is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

[0049] In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure

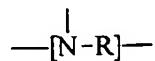
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is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified.

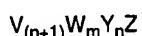
[0050] In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure

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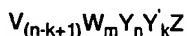


[0051] is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

[0052] The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



for linear amino-functional polymer and by the general formula



5 for cyclic amino-functional polymer. For the case of polyamines comprising rings, a Y' unit of the formula



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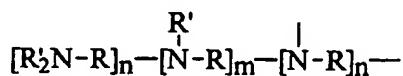
serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



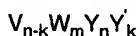
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that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula

20



25 therefore comprising no Z terminal unit and having the formula



wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention 30 comprise no rings.

[0052] In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula



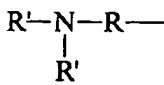
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that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 2 to 700, preferably 4 to 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

[0053] Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, Y' or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units or Y' units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

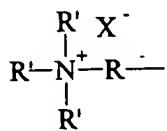
45 [0054] Modified primary amine moieties are defined as V "terminal" units having one of three forms:

a) simple substituted units having the structure:

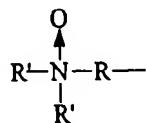


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55 b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and
c) oxidized units having the structure:

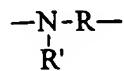


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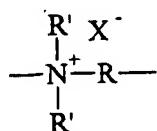
[0055] Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

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a) simple substituted units having the structure:



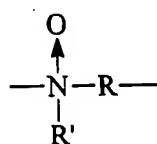
b) quaternized units having the structure:



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wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

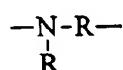


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[0056] Other modified secondary amine moieties are defined as Y' units having one of three forms:

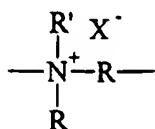
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a) simple substituted units having the structure:

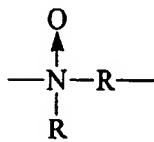


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b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and
c) oxidized units having the structure:



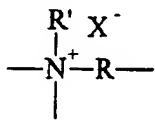
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20 [0057] Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

a) unmodified units having the structure:

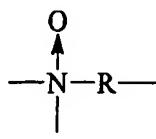


b) quaternized units having the structure:



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wherein X is a suitable counter ion providing charge balance; and
c) oxidized units having the structure:

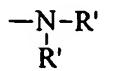


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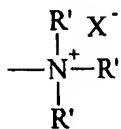
[0058] Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

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a) simple substituted units having the structure:

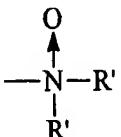


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

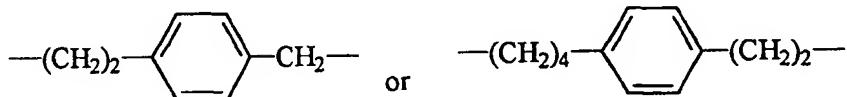


[0059] When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for R'. For example, a primary amine unit comprising one R' unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula $(HOCH_2CH_2)HN-$.

[0060] For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH₂. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units: The Z "terminal" unit can be substituted with any of the R' units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore R' cannot be a hydrogen.

[0061] The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxy-alkylene, and C₂-C₁₂ alkylidene units. The "oxy" R units are oxygen atoms. The R units may take any position on the R unit chain except the carbon atoms directly

alkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C₄-C₁₂ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C₈-C₁₂ dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



45 although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C₂-C₁₂ alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise -(R¹O)_xR⁵(OR¹)_x, -CH₂CH(OR²)CH₂O_z(R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -CH₂CH(OR²)CH₂-, -(R¹O)_xR¹-, and mixtures thereof Preferred R units are selected from the group consisting of C₂-C₁₂ alkylene, C₃-C₁₂ hydroxylalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -CH₂CH(OR²)CH₂-, -

(CH₂CH(OH)CH₂O)_yR¹(OCH₂CH(OH)CH₂)_w-, -(R¹O), R⁵(OR¹)_x-, more preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxy-alkylene, C₄-C₁₂ dihydroxyalkylene, -(R¹O)_xR¹-,-(R¹O)_xR⁵(OR¹)_x-,-(CH₂CH(OH)CH₂O)_yR¹(OCH₂CH(OH)CH₂)_w-, and mixtures thereof, even more preferred R units are C₂-C₁₂ alkylene, C₃ hydroxyalkylene, and mixtures thereof, most preferred are C₂-C₆ alkylene. The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

55 [0062] R¹ units are C₂-C₆ alkylene, and mixtures thereof, preferably ethylene.

R^2 is hydrogen, and $-(R^1O)_x B$, preferably hydrogen.

R^3 is C_1 - C_{18} alkyl, C_7 - C_{12} arylalkylene, C_7 - C_{12} alkyl substituted aryl, C_6 - C_{12} aryl, and mixtures thereof, preferably C_1 - C_{12} alkyl, C_7 - C_{12} arylalkylene, more preferably C_1 - C_{12} alkyl, most preferably methyl. R^3 units serve as part of R' units

described herein below.

[0063] R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, preferably C₁-C₁₀ alkylene, C₈-C₁₂ arylalkylene, more preferably C₂-C₈ alkylene, most preferably ethylene or butylene.

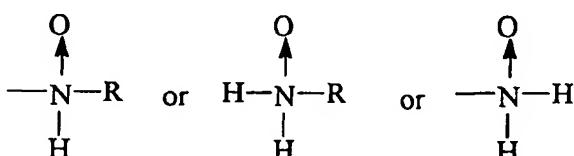
[0064] R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -C(O)(R⁴)C(O)-, -R¹(OR¹)-, -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-; -C(O)(R⁴)C(O)-, -CH₂CH(OH)CH₂-; R⁵ is preferably ethylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -R¹(OR¹)-, -CH₂CH(OH)CH₂-; -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-; more preferably -CH₂CH(OH)CH₂-; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene.

[0065] The preferred "oxy" R units are further defined in terms of the R¹, R², and R⁵ units. Preferred "oxy" R units 10 comprise the preferred R¹, R², and R⁵ units. The preferred cotton soil release agents of the present invention comprise at least 50% R¹ units that are ethylene. Preferred R¹, R², and R⁵ units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

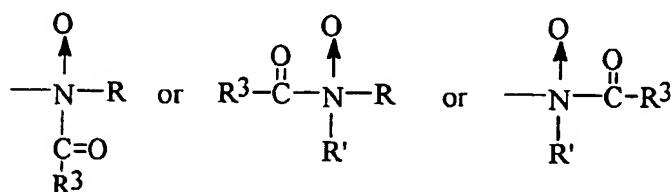
- i) Substituting more preferred R⁵ into -(CH₂CH₂O)_xR⁵(OCH₂CH₂)_x yields - (CH₂CH₂O)_xCH₂CHOCH₂(OCH₂CH₂)_x-.
- ii) Substituting preferred R¹ and R² into -(CH₂CH(OR²)CH₂O)_z(R¹O)_yR¹O(CH₂CH(OR²)CH₂)_w- yields - (CH₂CH(OH)CH₂O)_z(CH₂CH₂O)_yCH₂CH₂O(CH₂CH(OH)CH₂)_w-.
- iii) Substituting preferred R² into -CH₂CH(OR²)CH₂- yields -CH₂CH(OH)CH₂-.

20 R' units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, -(CH₂)_pPO₃M, -(R¹O)_mB, -C(O)R³, preferably hydrogen, C₂-C₂₂ hydroxyalkylene, benzyl, C₁-C₂₂ alkylene, -(R¹O)_mB, -C(O)R³, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, more preferably C₁-C₂₂ alkylene, -(R¹O)_xB, -C(O)R³, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, most preferably C₁-C₂₂ alkylene, -(R¹O)_xB, and -C(O)R³. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing R'. A most preferred R' unit is (R¹O)_xB.

R' units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



40 [0066] Additionally, R' units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the R' unit -C(O)R³ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

B is hydrogen, C₁-C₆ alkyl, -(CH₂)_qSO₃M, -(CH₂)_pCO₂M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q(CHSO₂M)CH₂SO₃M, -(CH₂)_pPO₃M, -PO₃M, preferably hydrogen, -(CH₂)_qSO₃M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q(CHSO₂M)CH₂SO₃M, more preferably hydrogen or -(CH₂)_qSO₃M.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies -(CH₂)_pCO₂M, and -(CH₂)_qSO₃M, thereby resulting in -(CH₂)_pCO₂Na, and -(CH₂)_qSO₃Na moieties.

More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one monovalent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a $-(CH_2)_pPO_3M$ moiety substituted with sodium atoms has the formula $-(CH_2)_pPO_3Na_3$. Divalent cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable mono-valent water soluble cations.

5 Preferred cations are sodium and potassium, more preferred is sodium.

[0067] X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine (I^-) or X can be any negatively charged radical such as sulfate (SO_4^{2-}) and methosulfate ($CH_3SO_3^-$).

10 [0068] The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; m has the value from 2 to 700, preferably from 4 to 400, n has the value from 0 to 350, preferably from 0 to 200; m + n has the value of at least 5.

[0069] Preferably x has a value lying in the range of from 1 to 20, preferably from 1 to 10.

15 [0070] The preferred amino-functional polymers of the present invention comprise polyamine backbones wherein less than 50% of the R groups comprise "oxy" R units, preferably less than 20%, more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

20 [0071] The most preferred amino-functional polymers which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C_2-C_{12} alkylene, preferred is C_2-C_3 alkylene, most preferred is ethylene.

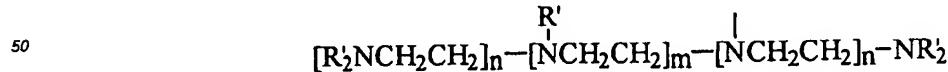
25 [0072] The amino-functional polymers of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethylenimines, therefore a sample of polyethylenimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

30 [0073] For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone.

35 [0074] Preferred amino-functional polymers of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

40 [0075] The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneimines (PAI's), preferably polyethylenimines (PEI's), or PEI's connected by moieties having longer R units than the parent PAI's or PEI's.

45 [0076] Preferred amine polymer backbones comprise R units that are C_2 alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



wherein R', m and n are the same as defined herein above. Preferred PEI's will have a molecular weight greater than 55 200 daltons.

[0077] The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxida-

tion.

[0078] These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

[0079] The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of R' groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

[0080] Commercially available amino-functional polymer suitable for use herein are poly(ethyleneimine) with a MW 1200, hydroxyethylated poly(ethyleneimine) from Polysciences, with a MW 2000, and 80% hydroxyethylated poly(ethyleneimine) from Aldrich. Still other suitable amino-functional polymer are oligoamine of low molecular weight. Most particularly preferred for use herein are oligoamines selected from 1,4-Bis(3-aminopropyl)piperazine, N,N'-Bis(3-aminopropyl)1,3-propanediamine, and mixtures thereof.

[0081] A typical amount of amino-functional polymer to be employed in the composition of the invention is preferably up to 90% by weight, preferably from 0.01% to 50% active by weight, more preferably from 0.1% to 20% by weight and most preferably from 0.5% to 15% by weight of the composition.

Crystal growth inhibitor component

[0082] The compositions of the present invention can further contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, and/or organo monophosphonic acid, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the compositions.

[0083] By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

[0084] The organo diphosphonic acid is preferably a C₁-C₄ diphosphonic acid, more preferably a C₂ diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

[0085] Still useful herein as crystal growth inhibitor are the organic monophosphonic acid Organo monophosphonic acid or one of its salts or complexes is also suitable for use herein as a CGI.

[0086] By organo monophosphonic acid it is meant herein an organo monophosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrants.

[0087] The organo monophosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred.

[0088] A preferred organo monophosphonic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer under the tradename of Bayhibit.

[0089] Still other components may be suitable for use in the present invention are as follows:

Soil Release Agent

[0090] Soil Release agents are desirably used in fabric care compositions of the present invention. Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

[0091] If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

[0092] The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, et al., issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451,

Scheibel et al., issued November 6; U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink et al., issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado et al., issued October 31, 1989; U.S. 4,956,447, Gosselink et al., issued September 11, 1990; U.S. 5,415,807 Gosselink et al., issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, et al..

5 [0093] Further suitable soil release agents are described in U.S. 4,201,824, Violand et al.; U.S. 4,240,918 Lagasse et al.; U.S. 4,525,524 Tung et al.; U.S. 4,579,681, Ruppert et al.; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

10 [0094] Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

[0095] When the composition is formulated as a softening composition, it will also comprise a fabric softening compound.

15 Fabric softening compound

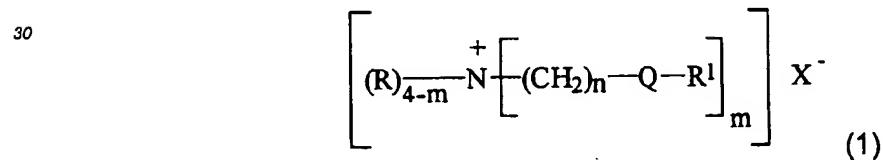
[0096] Typical levels of incorporation of the softening compound in the composition are of from 1% to 80% by weight, preferably from 5% to 75%, more preferably from 15% to 70%, and even more preferably from 19% to 65%, by weight of the composition.

20 [0097] Typical of the cationic softening components are the quaternary ammonium compounds or amine precursors thereof as defined hereinafter.

A)-Quaternary Ammonium Fabric Softening Active Compound

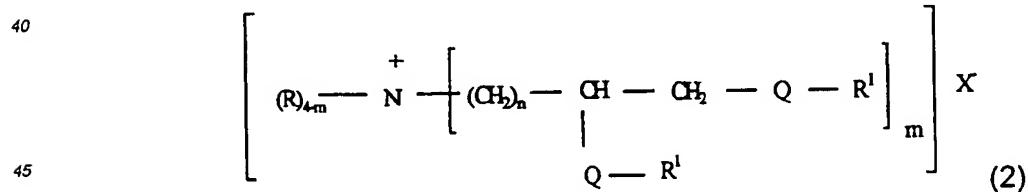
25 [0098]

(1) Preferred quaternary ammonium fabric softening active compound have the formula



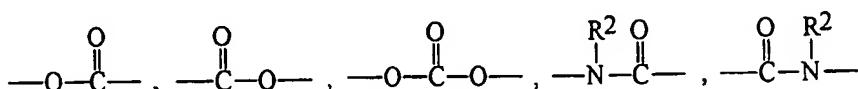
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or the formula:



wherein Q is a carbonyl unit having the formula:

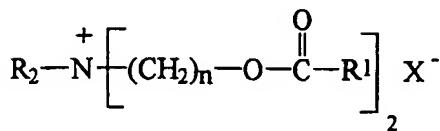
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55 each R unit is independently hydrogen, C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, and mixtures thereof, preferably methyl or hydroxy alkyl; each R¹ unit is independently linear or branched C₁₁-C₂₂ alkyl, linear or branched C₁₁-C₂₂ alkenyl, and mixtures thereof R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof X is an anion which is compatible with fabric softener actives and adjunct ingredients; the index m is from 1 to 4, preferably 2; the index n

is from 1 to 4, preferably 2.

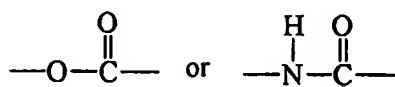
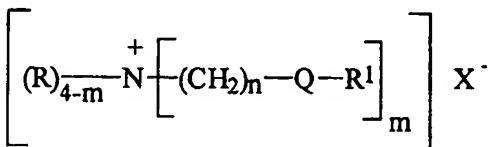
An example of a preferred fabric softener active is a mixture of quaternized amines having the formula:



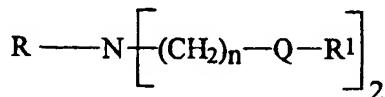
10 wherein R is preferably methyl; R¹ is a linear or branched alkyl or alkenyl chain comprising at least 11 atoms, preferably at least 15 atoms. In the above fabric softener example, the unit -O₂CR¹ represents a fatty acyl unit which is typically derived from a triglyceride source. The triglyceride source is preferably derived from tallow, partially hydrogenated tallow, lard, partially hydrogenated lard, vegetable oils and/or partially hydrogenated vegetable oils, such as, canola oil, safflower oil, peanut oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil, etc. and mixtures of these oils.

15 The preferred fabric softening actives of the present invention are the Diester and/or Diamide Quaternary Ammonium (DEQA) compounds, the diesters and diamides having the formula:

20 wherein R, R¹, X, and n are the same as defined herein above for formulas (1) and (2), and Q has the formula:

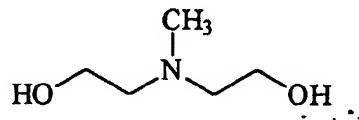


35 These preferred fabric softening actives are formed from the reaction of an amine with a fatty acyl unit to form an amine intermediate having the formula:

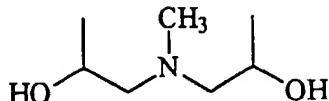


45 wherein R is preferably methyl, Q and R¹ are as defined herein before; followed by quaternization to the final softener active.

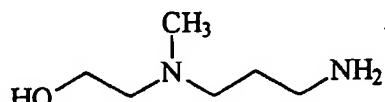
50 Non-limiting examples of preferred amines which are used to form the DEQA fabric softening actives according to the present invention include methyl bis(2-hydroxyethyl)amine having the formula:



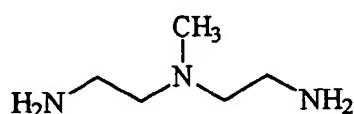
methyl bis(2-hydroxypropyl)amine having the formula:



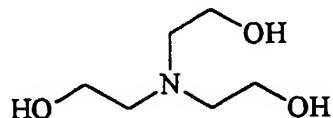
methyl (3-aminopropyl)(2-hydroxyethyl)amine having the formula:



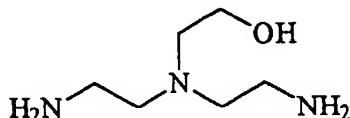
methyl bis(2-aminoethyl)amine having the formula:



triethanol amine having the formula:



di(2-aminoethyl) ethanolamine having the formula:



The counterion, $X^{(-)}$ above, can be any softener-compatible anion, preferably the anion of a strong acid, for example, chloride, bromide, methylsulfate, ethylsulfate, sulfate, nitrate and the like, more preferably chloride or methyl sulfate. The anion can also, but less preferably, carry a double charge in which case $X^{(-)}$ represents half a group.

Tallow and canola oil are convenient and inexpensive sources of fatty acyl units which are suitable for use in the present invention as R¹ units. The following are non-limiting examples of quaternary ammonium compounds suitable for use in the compositions of the present invention. The term "tallowyl" as used herein below indicates the R¹ unit is derived from a tallow triglyceride source and is a mixture of fatty alkyl or alkenyl units. Likewise, the use of the term canoyl refers to a mixture of fatty alkyl or alkenyl units derived from canola oil.

In the following table are described non-limiting examples of suitable fabric softener according to the above formula. In this list, the term "oxy" defines a



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unit, whereas the term "oxo" defines a -O- unit.

Table II

Fabric Softener Actives

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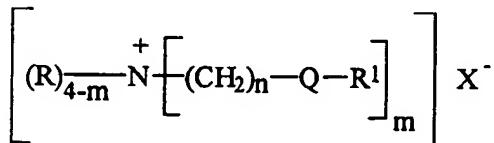
N,N-di(tallowyl-oxy-2-oxo-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
 N,N-di(canolyloxy-2-oxo-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
 15 N,N-di(tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 N,N-di(canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride
 N,N,N-tri(tallowyl-oxy-2-oxo-ethyl)-N-methyl ammonium chloride;
 N,N,N-tri(canolyloxy-2-oxo-ethyl)-N-methyl ammonium chloride;
 20 N-(tallowyloxy-2-oxo-ethyl)-N-(tallowyl)-N,N-dimethyl ammonium chloride;
 N-(canolyloxy-2-oxo-ethyl)-N-(canoly)-N,N-dimethyl ammonium chloride;
 1,2-di(tallowyloxy-oxo)-3-N,N,N-trimethylammoniopropane chloride; and
 25 1,2-di(canolyloxy-oxo)-3-N,N,N-trimethylammoniopropane chloride;
 and mixtures of the above actives.

Other examples of quaternary ammonium softening compounds are methylbis(tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate; these materials are available from Witco Chemical Company under the trade names Varisoft® 222 and Varisoft® 110, respectively.

Particularly preferred is N,N-di(tallowyl-oxy-2-oxo-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride, where the tallow chains are at least partially unsaturated.

The level of unsaturation contained within the tallow, canola, or other fatty acyl unit chain can be measured by the Iodine Value (IV) of the corresponding fatty acid, which in the present case should preferably be in the range of from 5 to 100 with two categories of compounds being distinguished, having a IV below or above 25.

Indeed, for compounds having the formula:



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derived from tallow fatty acids, when the Iodine Value is from 5 to 25, preferably 15 to 20, it has been found that a *cis/trans* isomer weight ratio greater than about 30/70, preferably greater than about 50/50 and more preferably greater than about 70/30 provides optimal concentrability.

For compounds of this type made from tallow fatty acids having a Iodine Value of above 25, the ratio of *cis* to *trans* isomers has been found to be less critical unless very high concentrations are needed. Other suitable examples of fabric softener actives are derived from fatty acyl groups wherein the terms "tallowyl" and "canoly" in the above examples are replaced by the terms "cocoyl, palmyl, lauryl, oleyl, ricinoleyl, stearyl, palmityl," which correspond to the triglyceride source from which the fatty acyl units are derived. These alternative fatty acyl sources can comprise either fully saturated, or preferably at least partly unsaturated chains.

As described herein before, R units are preferably methyl, however, suitable fabric softener actives are described by replacing the term "methyl" in the above examples in Table II with the units "ethyl, ethoxy, propyl, propoxy, isopropyl, butyl, isobutyl and t-butyl.

The counter ion, X, in the examples of Table II can be suitably replaced by bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the anion, X, is merely present as a counterion of the positively charged quaternary ammonium compounds. The scope of this invention is not considered limited to any particular anion.

For the preceding ester fabric softening agents, the pH of the compositions herein is an important parameter of the present invention. Indeed, it influences the stability of the quaternary ammonium or amine precursors compounds, especially in prolonged storage conditions.

The pH, as defined in the present context, is measured in the neat compositions at 20 °C. While these compositions are operable at pH of less than about 6.0, for optimum hydrolytic stability of these compositions, the neat pH, measured in the above-mentioned conditions, must preferably be in the range of from about 2.0 to about 5, preferably in the range of 2.5 to 4.5, preferably about 2.5 to about 3.5. The pH of these compositions herein can be regulated by the addition of a Bronsted acid.

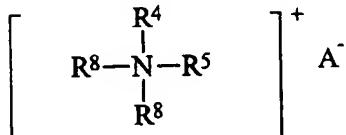
Examples of suitable acids include the inorganic mineral acids, carboxylic acids, in particular the low molecular weight (C_1-C_5) carboxylic acids, and alkylsulfonic acids. Suitable inorganic acids include HCl, H_2SO_4 , HNO_3 and H_3PO_4 . Suitable organic acids include formic, acetic, citric, methylsulfonic and ethylsulfonic acid. Preferred acids are citric, hydrochloric, phosphoric, formic, methylsulfonic acid, and benzoic acids.

As used herein, when the diester is specified, it will include the monoester that is normally present in manufacture. For softening, under no/low detergent carry-over laundry conditions the percentage of monoester should be as low as possible, preferably no more than about 2.5%. However, under high detergent carry-over conditions, some monoester is preferred. The overall ratios of diester to monoester are from about 100:1 to about 2:1, preferably from about 50:1 to about 5:1, more preferably from about 13:1 to about 8:1. Under high detergent carry-over conditions, the di/monoester ratio is preferably about 11:1. The level of monoester present can be controlled in the manufacturing of the softener compound.

Mixtures of actives of formula (1) and (2) may also be prepared.

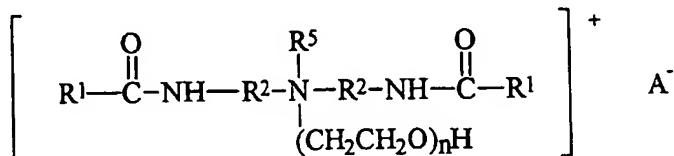
2)-Still other suitable quaternary ammonium fabric softening compounds for use herein are cationic nitrogenous salts having two or more long chain acyclic aliphatic C_8-C_{22} hydrocarbon groups or one said group and an arylalkyl group which can be used either alone or as part of a mixture are selected from the group consisting of

(i) acyclic quaternary ammonium salts having the formula:



wherein R^4 is an acyclic aliphatic C_8-C_{22} hydrocarbon group, R^5 is a C_1-C_4 saturated alkyl or hydroxyalkyl group, R^8 is selected from the group consisting of R^4 and R^5 groups, and A^- is an anion defined as above;

(ii) diamino alkoxylated quaternary ammonium salts having the formula:



wherein n is equal to 1 to about 5, and R^1 , R^2 , R^5 and A^- are as defined above;

(iii) mixtures thereof.

[0099] Examples of the above class cationic nitrogenous salts are the well-known dialkyldimethylammonium salts such as ditallowdimethylammonium chloride, ditallowdimethylammonium methylsulfate, di(hydrogenatedtallow)dimethylammonium chloride, distearyltrimethylammonium chloride, dibehenyldimethylammonium chloride. Di(hydrogenatedtallow)di methylammonium chloride and ditallowdimethylammonium chloride are preferred. Examples of commercially available dialkyldimethyl ammonium salts usable in the present invention are di(hydrogenatedtallow)dimethylammo-

5 nium chloride (trade name Adogen® 442), ditallowdimethylammonium chloride (trade name Adogen® 470, Praepagen® 3445), distearyl dimethylammonium chloride (trade name Arosurf® TA-100), all available from Witco Chemical Company. Dibehenyldimethylammonium chloride is sold under the trade name Kemamine Q-2802C by Humko Chemical Division of Witco Chemical Corporation. Dimethylstearylbenzyl ammonium chloride is sold under the trade names Varisoft® SDC by Witco Chemical Company and Ammonyx® 490 by Onyx Chemical Company.

B)-Amine Fabric Softening Active Compound

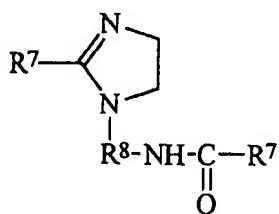
[0100] 10 Suitable amine fabric softening compounds for use herein, which may be in amine form or cationic form are selected from:

(i)- Reaction products of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof These reaction products are mixtures of several compounds in view of the multi-functional structure of the polyamines.

15 The preferred Component (i) is a nitrogenous compound selected from the group consisting of the reaction product mixtures or some selected components of the mixtures.

One preferred component (i) is a compound selected from the group consisting of substituted imidazoline compounds having the formula:

20



25

30 wherein R⁷ is an acyclic aliphatic C₁₅-C₂₁ hydrocarbon group and R⁸ is a divalent C₁-C₃ alkylene group.

Component (i) materials are commercially available as: Mazamide® 6, sold by Mazer Chemicals, or Ceranine® HC, sold by Sandoz Colors & Chemicals; stearic hydroxyethyl imidazoline sold under the trade names of Alkazine® ST by Alkaril Chemicals, Inc., or Schercozoline® S by Scher Chemicals, Inc.; N,N"-ditallowalkyldiethylenetriamine; 1-tallowamidoethyl-2-tallowimidazoline (wherein in the preceding structure R¹ is an aliphatic C₁₅-C₁₇ hydrocarbon group and R⁸ is a divalent ethylene group).

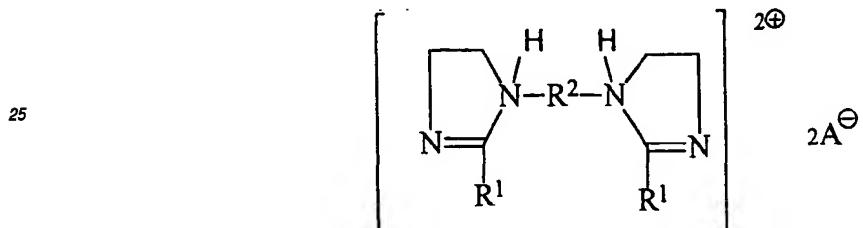
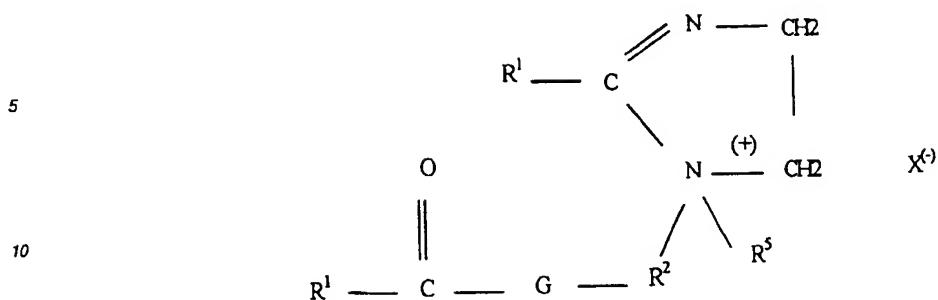
35 Certain of the Components (i) can also be first dispersed in a Bronsted acid dispersing aid having a pKa value of not greater than about 4; provided that the pH of the final composition is not greater than about 6. Some preferred dispersing aids are hydrochloric acid, phosphoric acid, or methylsulfonic acid.

Both N,N"-ditallowalkyldiethylenetriamine and 1-tallow(amidoethyl)-2-tallowimidazoline are reaction products of tallow fatty acids and diethylenetriamine, and are precursors of the cationic fabric softening agent methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate (see "Cationic Surface Active Agents as Fabric Softeners," R. R. Egan, Journal of the American Oil Chemicals' Society, January 1978, pages 118-121). N,N"-ditallow alkoyldiethylenetriamine and 1-tallowamidoethyl-2-tallowimidazoline can be obtained from Witco Chemical Company as experimental chemicals. Methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is sold by Witco Chemical Company under the tradename Varisoft® 475.

45 (ii)-softener having the formula:

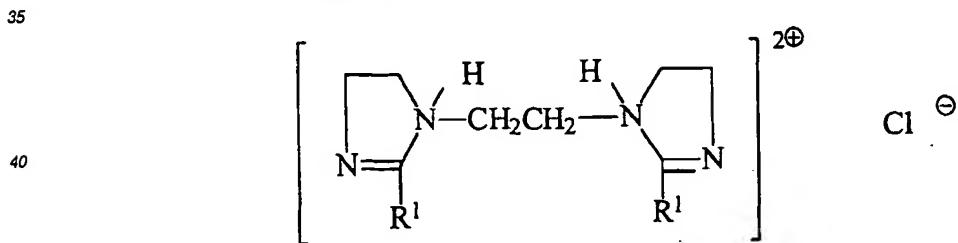
50

55



wherein R, R¹, R², and A⁻ are defined as above.

[0101] An example of Compound (iii) is the compound having the formula:



OPTIONAL INGREDIENTS(A)Liquid carrier

5 [0105] Another optional, but preferred, ingredient is a liquid carrier. The liquid carrier employed in the instant compositions is preferably at least primarily water due to its low cost, relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is preferably at least about 50%, most preferably at least about 60%, by weight of the carrier. Mixtures of water and low molecular weight, e.g., <about 200, organic solvent, e.g., lower alcohols such as ethanol, propanol, isopropanol or butanol are useful as the carrier liquid. Low molecular weight alcohols include
10 monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and higher polyhydric (polyols) alcohols.

(B)-Additional Solvents

15 [0106] The compositions of the present invention may comprise one or more solvents which provide increased ease of formulation. These ease of formulation solvents are all disclosed in WO 97/03169. This is particularly the case when formulating liquid, clear fabric softening compositions. When employed, the ease of formulation solvent system preferably comprises less than about 40%, preferably from about 10% to about 35%, more preferably from about 12% to about 25%, and even more preferably from about 14% to about 20%, by weight of the composition. The ease of formulation solvent is selected to minimize solvent odor impact in the composition and to provide a low viscosity to the final
20 composition. For example, isopropyl alcohol is not very effective and has a strong odor. n-Propyl alcohol is more effective, but also has a distinct odor. Several butyl alcohols also have odors but can be used for effective clarity/stability, especially when used as part of a ease of formulation solvent system to minimize their odor. The alcohols are also selected for optimum low temperature stability, that is they are able to form compositions that are liquid with acceptable low viscosities and translucent, preferably clear, down to about 40°F (about 4.4°C) and are able to recover after storage
25 down to about 20°F (about minus 6.7°C).

[0107] The suitability of any ease of formulation solvent for the formulation of the liquid, concentrated, preferably clear, fabric softener compositions herein with the requisite stability is surprisingly selective. Suitable solvents can be selected based upon their octanol/water partition coefficient (P) as defined in WO 97/03169.

30 [0108] The ease of formulation solvents herein are selected from those having a ClogP of from about 0.15 to about 0.64, preferably from about 0.25 to about 0.62, and more preferably from about 0.40 to about 0.60, said ease of formulation solvent preferably being at least somewhat asymmetric, and preferably having a melting, or solidification, point that allows it to be liquid at, or near room temperature. Solvents that have a low molecular weight and are biodegradable are also desirable for some purposes. The more assymetric solvents appear to be very desirable, whereas the highly
35 symmetrical solvents such as 1,7-heptanediol, or 1,4-bis(hydroxymethyl) cyclohexane, which have a center of symmetry, appear to be unable to provide the essential clear compositions when used alone, even though their ClogP values fall in the preferred range.

The most preferred ease of formulation solvents can be identified by the appearance of the softener vesicles, as observed via cryogenic electron microscopy of the compositions that have been diluted to the concentration used in the rinse. These dilute compositions appear to have dispersions of fabric softener that exhibit a more unilamellar appearance than conventional fabric softener compositions. The closer to uni-lamellar the appearance, the better the compositions seem to perform. These compositions provide surprisingly good fabric softening as compared to similar compositions prepared in the conventional way with the same fabric softener active.

40 [0109] Operable ease of formulation solvents are disclosed and listed below which have ClogP values which fall within the requisite range. These include mono-ols, C6 diols, C7 diols, octanediol isomers, butanediol derivatives, trimethylpentanediol isomers, ethylmethylpentanediol isomers, propyl pentanediol isomers, dimethylhexanediol isomers, ethyl-hexanediol isomers, methylheptanediol isomers, octanediol isomers, nonanediol isomers, alkyl glyceryl ethers, di(hydroxy alkyl) ethers, and aryl glyceryl ethers, aromatic glyceryl ethers, alicyclic diols and derivatives, C₃C₇ diol alkoxylation derivatives, aromatic diols, and unsaturated diols. Particularly preferred ease of formulation solvents include hexanediols such as 1,2-Hexanediol and 2-Ethyl-1,3-hexanediol and pentanediols such as 2,2,4-Trimethyl-1,3-pentanediol.

(C) Dispersibility Aids

55 [0110] Relatively concentrated compositions containing both saturated and unsaturated diester quaternary ammonium compounds can be prepared that are stable without the addition of concentration aids. However, the compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. These concentration aids which typically can be viscosity modifiers may be needed, or preferred, for ensuring stability under extreme conditions when particular

softener active levels are used. The surfactant concentration aids are typically selected from the group consisting of (1) single long chain alkyl cationic surfactants; (2) nonionic surfactants; (3) amine oxides; (4) fatty acids; and (5) mixtures thereof. These aids are described in WO 94/20597, specifically on page 14, line 12 to page 20, line 12, which is herein incorporated by reference.

5 When said dispersibility aids are present, the total level is from 2% to 25%, preferably from 3% to 17%, more preferably from 4% to 15%, and even more preferably from 5% to 13% by weight of the composition. These materials can either be added as part of the active softener raw material, (I), e.g., the mono-long chain alkyl cationic surfactant and/or the fatty acid which are reactants used to form the biodegradable fabric softener active as discussed hereinbefore, or added as a separate component. The total level of dispersibility aid includes any amount that may be present as part of component (I).

10 [0111] Inorganic viscosity/dispersibility control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, 15 sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition.

20 Alkylene polyammonium salts can be incorporated into the composition to give viscosity control in addition to or in place of the water-soluble, ionizable salts above. In addition, these agents can act as scavengers, forming ion pairs with anionic detergent carried over from the main wash, in the rinse, and on the fabrics, and may improve softness performance. These agents may stabilize the viscosity over a broader range of temperature, especially at low temperatures, compared to the inorganic electrolytes.

25 Specific examples of alkylene polyammonium salts include L-lysine monohydrochloride and 1,5-diammonium 2-methyl pentane dihydrochloride.

(D)-Stabilizers

30 [0112] Stabilizers can be present in the compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%, more preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions for the compositions and compounds stored in molten form. The use of antioxidants and reductive agent stabilizers is especially critical for low scent products (low perfume).

35 [0113] Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, 40 Eastman Chemical Products, Inc., as Tenox TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C₈-C₂₂) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171; Irganox® 1425; Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof 45 more preferably Irganox® 3125 alone. The chemical names and CAS numbers for some of the above stabilizers are listed in Table II below.

TABLE II

50	Antioxidant	CAS No.	Chemical Name used in Code of Federal Regulations
	Irganox® 1010	6683-19-8	Tetrakis (methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) methane
	Irganox® 1035	41484-35-9	Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)
55	Irganox® 1098	23128-74-7	N,N'-Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide)
	Irganox® B 1171	31570-04-4 23128-74-7	1:1 Blend of Irganox® 1098 and Irgafos® 168

TABLE II (continued)

Antioxidant	CAS N .	Chemical Name used in Cod of Federal Regulations
Irganox® 1425	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)
Irganox® 3114	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)
Irganox® 3125 acid	34137-09-2	3,5-Di-tert-butyl-4-hydroxy-hydrocinnamic triester with 1,3,5-tris(2-hydroxyethyl)-S-triazine-2,4,6-(1 H, 3H, 5H)-trione
Irgafos® 168	31570-04-4	Tris(2,4-di-tert-butyl-phenyl)phosphite

10

[0114] Examples of reductive agents include sodium borohydride, hypophosphorous acid, Irgafos® 168, and mixtures thereof.

15 (E)-Bactericides

[0115] Examples of bactericides used in the compositions of this invention include glutaraldehyde, formaldehyde, 2-bromo-2-nitro-propane-1,3-dial sold by Inolex Chemicals, located in Philadelphia, Pennsylvania, under the trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm 20 and Haas Company under the trade name Kathon 1 to 1,000 ppm by weight of the agent.

(F)-Perfume

[0116] The present invention can contain a perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

[0117] As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are 30 also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

[0118] Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpineol; 3,7-dimethyl-cis-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-trans-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecetyl propionate; tricyclodecetyl acetate; anisaldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

[0119] Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methyl-ether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate; methylphenylcarbonyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecanoic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-cyclododeca-45 trien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; olibanum resinoid labdanum; vetivert; copaiba balsam; fir balsam; and condensation products of hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.

More examples of perfume components are geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; neryl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl ben-

zoate; styrryl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbonyl methylphenylcarbonyl acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(*p*-tert-butylphenyl)-propanal; 2-methyl-3-(*p*-isopropylphenyl)-propanal; 3-(*p*-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydro-
5 pyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentyl-cyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methylether; isolongifolanone; aubepine
10 nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionomes; irones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

10 [0120] The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

[0121] Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, iso-propanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a
15 homogeneous perfume solution.

[0122] Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

[0123] Perfume ingredients may also be suitably added as releasable fragrances, for example, as pro-perfumes or
20 pro-fragrances as described in U.S. 5,652,205 Hartman et al., issued July 29, 1997, WO95/04809, WO96/02625, PCT US97/14610 filed 19 August 1997 and claiming priority of 19 August 1996, and EP-A-0,752,465, incorporated herein by reference.

(G)-Enzyme

25 [0124] The compositions and processes herein can optionally employ one or more enzymes such as lipases, proteases, cellulase, amylases and peroxidases. A preferred enzyme for use herein is a cellulase enzyme. Indeed, this type of enzyme will further provide a color care benefit to the treated fabric. Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307 discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. Other suitable cellulases are also disclosed in WO 91/17243 to Novo, WO 96/34092, WO 96/34945 and EP-A-0,739,982. In practical terms for current commercial preparations, typical amounts are up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition.
30 Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. In the particular cases where activity of the enzyme preparation can be defined otherwise such as with cellulases, corresponding activity units are preferred (e.g. CEVU or cellulase Equivalent Viscosity Units). For instance, the compositions of the present invention can contain cellulase enzymes at a level equivalent to an activity from 0.5 to 1000 CEVU/gram of composition. Cellulase enzyme preparations used for the purpose of formulating the compositions of this invention typically have an activity comprised between 1,000 and 10,000 CEVU/gram in liquid form, around 1,000 CEVU/gram in solid form.

Other Optional Ingredients

45 [0125] The present invention can include optional components conventionally used in textile treatment compositions, for example: brighteners, chlorine scavengers such the non-polymeric one described in EP-A-0,841,391, colorants; surfactants; anti-shrinkage agents; fabric crisping agents; spotting agents; germicides; fungicides; anti-oxidants such as butylated hydroxy toluene, anti-corrosion agents, antifoam agents, sun-protection agents such as described in EP-A-0,773,987, and the like.

50 [0126] The present invention can also include other compatible ingredients, including those as disclosed in WO96/02625, WO96/21714, and WO96/21715, and dispersible polyolefin such as Velustrol® as disclosed in co-pending application PCT/US 97/01644, and the like. The present invention can also contain optional chelating agents such as ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt (EDDS).

55 [0127] Still other various optional adjunct ingredients may also be used to provide fully-formulated detergent compositions. Typical of such conventional detergents ingredients include detergents surfactants, builders, bleaching compounds, and mixtures thereof, such as described in WO 98/20098.

Form of the composition

[0128] The colour care composition can take a variety of physical forms including liquid such as aqueous or non-aqueous compositions and solid forms such as solid particulate forms.

5 Such compositions may be applied onto a substrate such as a dryer sheet product, used as a rinse added product, or as a spray or foam product.

Method of use

10 [0129] In another aspect of the invention, there is provided a method for preventing or reducing the colour fading of fabrics which comprises the steps of contacting the fabric with a divalent salt or composition of the invention. Also herein provided is the use of said divalent salt to prevent or reduce the colour fading of fabrics

[0130] By the present method and/use, it has surprisingly been found that the treated fabric had better fabric appearance, especially in term of their color protection, compared to fabrics which had been treated with either no divalent salt.

15 [0131] Preferably, the method is performed in a domestic process. By "domestic process", it is meant any step conventional to domestic laundering such as soaking, washing, rinsing, and/or spraying as well as by means of a dryer sheet onto which is adsorbed the composition.

[0132] Preferably, the contacting occurs in the step of a laundering process, preferably a rinse step of a laundry process, which more preferably occurs at a temperature range below 30°C, preferably between 5 and 25°C.

20 [0133] The invention is illustrated in the following non limiting examples, in which all percentages are on a weight basis unless otherwise stated.

[0134] In the examples, the abbreviated component identifications have the following meanings:

DEQA :	Di-(tallowyl-oxy-ethyl) dimethyl ammonium chloride
25 DOEQA :	Di-(oleyloxyethyl) dimethyl ammonium methylsulfate
DTDMAC :	Ditallow dimethylammonium chloride
DHEQA :	Di-(soft-tallowyl-oxy-ethyl) hydroxyethyl methyl ammonium methylsulfate
DTDMAMS :	Ditallow dimethyl ammonium methylsulfate
SDASA :	1:2 Ratio of stearyl(dimethyl amine:triple-pressed stearic acid
30 Glycosperse S-20 :	Polyethoxylated sorbitan monostearate available from Lonza
Clay :	Calcium Bentonite Clay, Bentonite L, sold by Southern Clay Products
PEG :	Polyethylene Glycol 4000
PEI 1800 E1 :	Ethoxylated polyethylene imine (MW 1800, at 50% active) as synthesised in Synthesis example 1
35 PEI 1800 E3 :	Ethoxylated polyethylene imine (MW 1800, at 50% active) as synthesised as per Synthesis example 1
PEI 1200 E1 :	Ethoxylated polyethylene imine (MW 1200, at 50% active in water) as synthesised in Synthesis example 2
40 PEI 1200 E4 :	Ethoxylated polyethylene imine (MW 1200, at 50% active in water) as synthesised per Synthesis example 2
Dye Fix 1 :	Cellulose reactive dye fixing agent available under the tradename Indosol CR from Clariant
Dye Fix 2 :	Cellulose reactive dye fixing agent available under the tradename Rewin WBS from CHT R. Beilich
45 Divalent salt 1	Magnesium sulphate
Divalent salt 2	Magnesium chloride
Divalent salt 3	Calcium chloride
LAS :	Sodium linear C ₁₁ -13 alkyl benzene sulfonate
CxyAS :	Sodium C _{1x} -C _{1y} alkyl sulfate
CxyEzS :	Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide
50 CxyEz :	C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
APA :	C ₈ - C ₁₀ amido propyl dimethyl amine
CFAA :	C ₁₂ -C ₁₄ (coco) alkyl N-methyl glucamide
TFAA :	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
55 TPKFA :	C ₁₂ -C ₁₄ topped whole cut fatty acids
Citric acid :	Anhydrous citric acid
Borate :	Sodium borate
Protease :	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S

	under the tradename Savinase
Alcalase :	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
Cellulase :	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
5 Amylase :	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
Lipase :	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
Endolase :	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
10 DTPA :	Diethylene triamine pentaacetic acid
DTPMP :	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
Brightener 1 :	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2 :	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2:2'-disulfonate
15 HEDP :	1,1-hydroxyethane diphosphonic acid
TEPAE :	Tetraethylenepentaamine ethoxylate
PVNO :	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
SRP 1 :	Anionically end capped poly esters
SRP 2 :	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
20 Silicone antifoam :	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
Opacifier :	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
Polycarboxylic :	Polycarboxylic compound marketed by BASF under the tradename Sokalan CP 10
25 Glycolic :	Glycolic acid
Polymer I	Polyvinylpyrrolidone K90 available under the tradename Luviskol K90 from BASF.
Bayhibit AM :	2-phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer
pH :	Measured as a 1% solution in distilled water at 20°C.

30 Synthesis Example 1 -Preparation of PEI 1800 E₁

[0135] Step A)-The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

35 A 750 g portion of polyethylenimine (PEI) (Nippon Shokubai, Epomin SP-018 having a listed average molecular weight of 1800 equating to 0.417 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 40 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 45 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

[0136] Step B)- The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) 50 through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C. The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

[0137] In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

[0138] If a PEI 1800 E₇ is desired, the following step of catalyst addition will be included between Step A and B. 55 Vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored

along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

5 Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

10 The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles).

15 [0139] Other preferred examples such as PEI 1800 E3, PEI 1800 E4, PEI 1800 E15 and PEI 1800 E20 can be prepared by the above method by adjusting the reaction time and the relative amount of ethylene oxide used in the reaction.

Synthesis Example 2 - Preparation of PEI 1200 E₁

20 [0140] Step A)-The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

25 A 750 g portion of polyethylenimine (PEI) (having a listed average molecular weight of 1200 equating to about 0.625 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the 30 autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been 35 charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

[0141] Step B)- The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

40 The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

[0142] If a PEI 1200 E₇ is desired, the following step of catalyst addition will be included between Step A and B.

[0143] Vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% 45 sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

50 Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles).

5 [0144] Other preferred examples such as PEI 1200 E2, PEI 1200 E4, PEI 1200 E15 and PEI 1200 E20 can be prepared by the above method by adjusting the reaction time and the relative amount of ethylene oxide used in the reaction.

Example 1

10 [0145] The following fabric care compositions are in accordance with the present invention

		Active (levels in %)	I	II	III	IV	V	VI	VII
15		PEI 1200 E1	10	9	8	7	6	2	4
		Dye fix 2	2.5	2.5	1	2	3	2	3
20		Divalent salt 1	5	6	7	8	10	2	15
		DEQA	-	-	-	-	-	25	-
25		HEDP	1	0.2	0.4	0.5	0.5	0.1	1
		ammonium chloride	-	-	-	-	-	-	0.25
		SRP1	-	-	-	-	-	-	2
		Water and minors to balance to 100							

30

		Active (levels in %)	VIII	IX	X	XI	XII	XIII	XIV
35		PEI 1200 E4	10	9	8	7	6	2	4
		Dye fix 1	2.5	2.5	1	2	3	2	3
40		Divalent salt 2	5	6	7	8	10	2	15
		DTDMAC						25	
45		HEDP	1	0.2	0.4	0.5	0.5	0.1	1
		ammonium chloride	-	-	-	-	-	-	0.25
		SRP1	-	-	-	-	-	-	2
		Water and minors to balance to 100							

50

	XV	XVI	XVII	XVIII	
55	Divalent salt 1	5	15	2	2
	PEI 1800 E4	-	-	15	-
	Polymer I	-	-	-	5

(continued)

	XV	XVI	XVII	XVIII
DEQA	5	-	-	-
Dye fix 1	-	2.5	-	-
Bayhibit AM	2	-	-	-
Cellulase	-	0.1	-	0.5
Perfume	0.15	0.3	0.1	0.4
Water and minors	Balance	Balance	Balance	Balance

Example 2

15

[0146] The following compositions for use as dryer-added sheets are in accordance with the invention

20

	I	II	III	IV	V	VI
DOEQA	40	25	-	-	-	-
DHEQA	-	-	20	-	-	-
DTDMAMS	-	-	-	20	12	60
SDASA	30	30	20	30	20	-
Glycosperse S-20	-	-	10	-	-	-
Glycerol Monostearate	-	-	-	20	10	-
Clay	4	4	3	4	4	-
Perfume	0.7	1.1	0.7	1.6	2.6	1.4
PEI 1800 E1	-	5	-	-	-	-
PEI 1200 E1	-	-	4	2.2	-	-
PEI 1800 E3	2	-	-	-	5	7.0
Dye fix 2	2	5	4	2.2	5	3
Divalent salt 1	5	3	10	2	5	6
HEDP	0.2	-	0.5	-	-	0.7
Glycolic	-	0.2	-	0.2	-	-
Polycarboxylic	-	0.2	-	-	0.4	-
Stearic acid to balance						

Example 3

50

[0147] The following liquid detergent formulations were prepared in accord with the invention (levels are given as parts per weight).

55

	I	II	III	IV	V
LAS	11.5	8.8	-	3.9	-

(continued)

	I	II	III	IV	V	
5	C25E2.5S	-	3.0	18.0	-	16.0
10	C45E2.25S	11.5	3.0	-	15.7	-
15	C23E9	-	2.7	1.8	2.0	1.0
20	C23E7	3.2	-	-	-	-
25	CFAA	-	-	5.2	-	3.1
30	TPKFA	1.6	-	2.0	0.5	2.0
35	Citric acid (50%)	6.5	1.2	2.5	4.4	2.5
40	Calcium formate	0.1	0.06	0.1	-	-
45	Sodium formate	0.5	0.06	0.1	0.05	0.05
50	Sodium cumene sulfonate	4.0	1.0	3.0	1.18	-
55	Borate	0.6	-	3.0	2.0	2.9
60	Sodium hydroxide	5.8	2.0	3.5	3.7	2.7
65	Ethanol	1.75	1.0	3.6	4.2	2.9
70	1, 2 propanediol	3.3	2.0	8.0	7.9	5.3
75	Monoethanolamine	3.0	1.5	1.3	2.5	0.8
80	TEPAE	1.6	-	1.3	1.2	1.2
85	Protease	1.0	0.3	1.0	0.5	0.7
90	Lipase	-	-	0.1	-	-
95	Cellulase	-	-	0.1	0.2	0.05
100	Amylase	-	-	-	0.1	-
105	SRP1	0.2	-	0.1	-	-
110	DTPA	-	-	0.3	-	-
115	Divalent salt 1	2	3	4	5	4
120	PVNO	-	-	0.3	-	0.2
125	Perfume	0.4	0.4	0.4	0.4	0.4
130	Brightener 1	0.2	0.07	0.1	-	-
135	Silicone antifoam	0.04	0.02	0.1	0.1	0.1
140	Water/minors					

Example 4

[0148] The following liquid detergent formulations were prepared in accord with the invention (levels are given in parts per weight):

50

	I	II	III	IV	V	VI	VII	VIII
55	LAS	10.0	13.0	9.0	-	25.0	-	-
60	C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0
65	C25E3S	1.0	-	-	3.0	-	2.0	4.0

(continued)

	I	II	III	IV	V	VI	VII	VIII	
5	C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0	
APA	-	1.4	-	-	3.0	1.0	2.0	-	
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0	
10	Citric acid	2.0	3.0	1.0	1.5	1.0	1.0	1.0	
Dodeceny/tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-	
Rape seed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-	
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0	
15	1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0	
Triethanolamine	-	-	8.0	-	-	-	-	-	
20	TEPAE	0.5	-	0.5	0.2	-	-	0.4	0.3
DTPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-	
Divalent salt 2	2	3	4	5	4	5	5	5	
25	Protease	0.5	0.5	0.4	0.25	-	0.5	0.3	0.6
Alcalase	-	-	-	-	1.5	-	-	-	
Lipase	-	0.10	-	0.01	-	-	0.15	0.15	
30	Amylase	0.25	0.25	0.6	0.5	0.25	0.9	0.6	0.6
Cellulase	-	-	-	0.05	-	-	0.15	0.15	
Endolase	-	-	-	0.10	-	-	0.07	-	
SRP2	0.3	-	0.3	0.1	-	-	0.2	0.1	
35	Boric acid	0.1	0.2	1.0	2.0	1.0	1.5	2.5	2.5
Calcium chloride	-	0.02	-	0.01	-	-	-	-	
Bentonite clay	-	-	-	-	4.0	4.0	-	-	
40	Brightener 1	-	0.4	-	-	0.1	0.2	0.3	-
Sud suppressor	0.1	0.3	-	0.1	0.4	-	-	-	
Opacifier	0.5	0.4	-	0.3	0.8	0.7	-	-	
Perfume	-	0.2	0.2	0.4	0.4	0.4	0.4	0.4	
45	Water/minors								
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2	

Example 5

50 [0149] The following liquid detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

55

	I	II
LAS	27.6	18.9

(continued)

	I	II	
5	C45AS	13.8	5.9
10	C13E8	3.0	3.1
	Oleic acid	3.4	2.5
15	Citric acid	5.4	5.4
	Sodium hydroxide	0.4	3.6
20	Calcium formate	0.2	0.1
	Sodium formate	-	0.5
	Ethanol	7.0	-
25	Monoethanolamine	16.5	8.0
	1,2 propanediol	5.9	5.5
	Xylene sulfonic acid	-	2.4
30	TEPAE	1.5	0.8
	Protease	1.5	0.6
	PEG	-	0.7
	Brightener 2	0.4	0.1
35	Perfume	0.5	0.3
	Divalent salt 1	3	3
	Water/minors		

Claims

1. A colour care composition comprising:

35 i)- a dye fixing agent, and
 ii)- a divalent salt.

2. A composition according to Claim 1, wherein said dye fixing agent is a cationic dye fixing agent.

40 3. A composition according to Claim 1, wherein said dye fixing agent is cellulose reactive dye fixing agent, preferably the cellulose reactive dye fixing agent is a product containing the reactive group of the reactive dye classes selected from halogeno-triazine products, vinyl sulphones compounds, epichlorhydrine derivatives, hydroxyethylene urea derivatives, formaldehyde condensation products, polycarboxylates, glyoxal and glutaraldehyde derivatives and mixtures thereof.

45 4. A composition according to Claim 3, wherein said cellulose reactive dye fixing agent is a formaldehyde condensation product selected from the condensation products derived from formaldehyde and a group selected from an amino-group, an imino-group, a phenol group, an urea group, a cyanamide group and an aromatic group.

50 5. A composition according to any one of Claims 1-4, wherein said dye fixing agent is present in an amount of 0.01% to 50% by weight, preferably from 0.01% to 25% by weight of the composition.

6. A composition according to any one of Claims 1-5, wherein said divalent salt is made of earth alkaline metal salts, preferably selected from magnesium, calcium and mixtures thereof.

55 7. A composition according to any one of Claims 1-6, wherein said divalent salt is selected from magnesium sulphate, magnesium bicarbonate, magnesium chloride, magnesium borate, magnesium citrate, and mixtures thereof, more preferably are selected from magnesium sulphate, magnesium chloride and mixtures thereof.

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8. A composition according to any one of Claims 1-6, wherein said divalent salt is present in an amount of from 0.01% to 90% by weight, preferably from 0.5% and 90%, more preferably between 1% and 20%, most preferably between 3% and 10%, by weight of the composition.
- 5 9. The use of a divalent salt to prevent or reduce the colour fading of fabrics.
10. A method for preventing or reducing the colour fading of fabrics which comprises the steps of contacting the fabric with a divalent salt or composition as defined in any one of Claims 1-9.
- 10 11. A method according to Claim 10, wherein said method is performed in a domestic process.
12. A method according to Claim 11, wherein said method is performed in a rinse process.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 98 87 0174

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	WO 98 12295 A (PROCTER & GAMBLE) 26 March 1998	1,2,5-7, 10-12	C11D7/10 C11D3/02
Y	* page 4, line 31 - page 5, line 30 *	1-4	
A	* page 34, line 16 - line 34 *	8,9	
	* page 36, line 14 - line 17; example 1E *	---	
Y	WO 96 27649 A (PROCTER & GAMBLE) 12 September 1996 * page 1, paragraph 1 * * page 3, paragraph 3; claim 1 *	1-4	
X	EP 0 811 680 A (PROCTER & GAMBLE) 10 December 1997	1,2,5-7, 10-12	
A	* page 2, line 51 - page 3, line 32; claims 1,7 *	3,4,8,9	
	* page 8, line 1 - line 18; claims 1,7; example 1 *	---	
X	WO 98 17758 A (PROCTER & GAMBLE) 30 April 1998	1,2,5,6, 10-12	
A	* page 3, paragraph 4 - page 4, paragraph 2 * * page 11, paragraph 4 * * page 40, paragraph 1; example 1A *	3,4,7-9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	WO 98 29529 A (PROCTER & GAMBLE) 9 July 1998 * page 5, paragraph 3 - page 7, paragraph 1; claim 1; example 1 *	1-12	C11D
D,A	EP 0 462 806 A (UNILEVER) 27 December 1991 * page 3, line 2 - line 18 *	1-12	
A	WO 97 32956 A (PROCTER & GAMBLE) 12 September 1997 * abstract * * page 29, paragraph 1 - paragraph 2; claims 1,6; example 7W *	1,10-12	
<p>The present search report has been drawn up for all claims</p>			
Place of search THE HAGUE	Date of completion of the search 23 November 1998	Examiner Saunders, T	
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			